

## PATENT ABSTRACTS OF JAPAN

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(54) PRODUCTION OF THERMOPLASTIC POLYESTER RESIN FOAM

## (57)Abstract:

PURPOSE: To produce continuously the title foam which has a cell size of 50 $\mu$ m or lower, high mechanical strengths, and almost smooth surfaces.

CONSTITUTION: The title foam is produced by allowing a thermoplastic polyester resin to absorb an inert gas under pressure, increasing the degree of crystallization of the resin to 30% or higher while preventing its blowing, and thermally blowing it under normal pressure.

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CLAIMS

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[Claim(s)]

[Claim 1] The manufacture approach of the thermoplastic-polyester system resin foam characterized by to provide the process which makes non-reactivity gas contain in thermoplastic-polyester system resin under pressurization, the process which makes the degree of crystallinity of thermoplastic-polyester system resin 30% or more while controlling foaming of the thermoplastic-polyester system resin containing non-reactivity gas, and the process which makes the thermoplastic-polyester system resin containing non-reactivity gas heat and foam to the bottom of pressureless.

[Claim 2] The manufacture approach of the thermoplastic polyester system resin foam according to claim 1 characterized by making the degree of crystallinity of thermoplastic polyester system resin 30% or more while controlling foaming by making thermoplastic polyester system resin immersed in an organic solvent after making it contain before making non-reactivity gas contain in thermoplastic polyester system resin or.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the manufacture approach of thermoplastic polyester system resin foam suitable as ingredients, such as heat insulating material and a heat insulator.

[0002]

[Description of the Prior Art] Before, various approaches are developed as the manufacture approach of polyester system resin foam.

[0003] After degree of crystallinity infiltrates a foaming agent into 10% or less of polyester resin, the approach of making it foam at 150-200 degrees C is indicated by JP,60-87043,A. As a reason for specifying the degree of crystallinity of resin in this official report as 10% or less, if degree of crystallinity is high, it is indicated that it is because the rate of impregnation of a foaming agent becomes low. Moreover, under foaming agent sinking in and foaming do not change, but, as for the degree of crystallinity of resin, it is indicated that crystallization advances after foaming termination. However, it is difficult to obtain detailed air bubbles, such as 50 micrometers or less, by this approach, in order the rigidity of resin is small since the degree of crystallinity of the resin at the time of foaming is as low as 10% or less, and air bubbles are large at the aforementioned foaming temperature and to grow up. In fact, in the specification, it is indicated that the diameter of air bubbles of the obtained foam is about 300 micrometers.

[0004] After carrying out melting of the aromatic polyester containing a foaming agent to JP,61-48411,B and extruding from a die, the method of manufacturing string-like aromatic polyester foam is indicated by what (it specifically cools slowly) is processed so that it may become 30% or more of degree of crystallinity of attainment degree of crystallinity.

[0005] After carrying out melting of the polyester system resin containing a foaming agent and extruding it, the approach of making the degree of crystallinity of the resin in an epidermis part 30% or less is indicated by quenching a front face compulsorily by JP,3-199243,A.

[0006] After extruding the viscous large melting resin which carried out melting of the polyester system resin (the melting property modifier is added) containing a foaming agent to JP,2-265725,A, the continuous approach of manufacturing is indicated for degree of crystallinity by quenching in 20% or less of polyester system resin foaming sheet.

[0007] The method of manufacturing polyester system resin foam is indicated by quenching, heating degree of crystallinity to it further, and making it to consider as 30% or less and it carry out post expansion, after carrying out melting of the polyester system resin containing a foaming agent and extruding it in JP,3-134037,A.

[0008] The manufacture approach of the polyester system resin foam which mixes and carries out extrusion foaming of thermoplastic polyester system resin, a melting property modifier, and the foaming agent to JP,3-266911,A, heats them to it, carries out post expansion to it, and carries out the amount of cold heat of crystallization of a post expansion object in 3000J/mol or less is indicated. In addition, since the amount of cold heat of crystallization is a fundamental value when computing the degree of crystallinity of crystalline polymer, this approach is equivalent to having essentially specified degree of crystallinity. When this invention persons

convert the aforementioned amount of cold heat of crystallization into degree of crystallinity by estimate, degree of crystallinity is about 10%.

[0009] However, since foaming is advanced at the same time each of these approaches extrudes the resin of the fused amorphous state into atmospheric air from a die, it is difficult to make the diameter of air bubbles small, and the foam which has detailed air bubbles, such as 50 micrometers or less, is not obtained. Moreover, the degree of crystallinity of the foam from which all were obtained is only specified, and the degree of crystallinity of the resin in the condition that the foaming agent sank in is not specified.

[0010]

[Problem(s) to be Solved by the Invention] As stated above, by the conventional approach, the diameter of air bubbles contains air bubbles 50 micrometers or less, and a mechanical strength is large, and it is difficult to obtain continuously the polyester system resin foam which does not almost have irregularity in a front face.

[0011] The diameter of air bubbles is 50 micrometers or less, and the purpose of this invention has a large mechanical strength, and is to offer the approach that the polyester system resin foam which does not almost have irregularity in a front face can be manufactured continuously.

[0012]

[Means for Solving the Problem] The manufacture approach of the thermoplastic polyester system resin foam of this invention The process which makes non-reactivity gas contain in thermoplastic polyester system resin under pressurization (henceforth "the 1st process"), Controlling foaming of the thermoplastic polyester system resin containing non-reactivity gas It has the process (henceforth "the 2nd process") which makes the degree of crystallinity of thermoplastic polyester system resin 30% or more, and the process (henceforth "the 3rd process") which makes the thermoplastic polyester system resin containing non-reactivity gas heat and foam to the bottom of pressureless.

[0013] Hereafter, the manufacture approach of this invention is explained to a detail for every process.

[0014] The 1st process is a process which makes non-reactivity gas contain in thermoplastic polyester system resin under pressurization. As thermoplastic polyester system resin, polyethylene terephthalate (it omits Following PET), polybutylene terephthalate, poly naphthalene terephthalate, etc. are mentioned. As non-reactivity gas, inert gas, such as an argon, nitrogen, and a carbon dioxide, air, or these mixed gas is mentioned. Also among these, a carbon dioxide is desirable, using the content to the inside of thermoplastic polyester system resin as the gas which can increase most.

[0015] This processing is performed by pouring non-reactivity gas into the thermoplastic polyester system resin of the melting condition pressurized for example, in the extruder from the barrel middle. Moreover, the approach of making non-reactivity gas containing may be used by leading the polyester system resin Plastic solid extruded for example, in the shape of a sheet from the extruder in the pressurized container filled with non-reactivity gas through mechanical seal etc. Especially pressurization conditions are 10kg/cm<sup>2</sup> at a room temperature, in order to increase the content of the non-reactivity gas to the inside of thermoplastic polyester system resin, although not limited. Considering as the above pressure is desirable.

[0016] The 2nd process is a process which makes the degree of crystallinity of the thermoplastic polyester system resin 30% or more, controlling foaming of the thermoplastic polyester system resin containing non-reactivity gas.

[0017] Since the thermoplastic polyester system resin of the melting condition containing non-reactivity gas is extruded into atmospheric air as it is by the conventional approach, it is very difficult to obtain the foam which the pressure applied to resin at the moment of come out of an extruder is released, and foaming by rapid expansion of non-reactivity gas takes place in the extruder outlet section, and has detailed air bubbles.

[0018] By the approach of this invention, without releasing the pressure to which the polyester system resin extruded, for example from the extruder was added by resin, as it is, it leads to another pressurized room, and by carrying out cooling solidification, foaming is made to control and the degree of crystallinity of the resin Plastic solid which contained non-reactivity gas in

this condition is made 30% or more.

[0019] In this invention, having limited degree of crystallinity with 30% or more is based on the following reasons. According to examination of this invention persons, when crystalline polyester system resin makes non-reactivity gas contain, crystallization advances. Drawing 1 is carbon dioxide gas as non-reactivity gas to the polyester system resin of an amorphous state 60kg/cm<sup>2</sup>. The relation of the gas sinking-in time amount and the degree of crystallinity at the time of making it contain is shown. Degree of crystallinity changes rapidly near 25 to 30%, and changes gently at 20% or less and 35% or more. And although the gas content was the same, two or more samples from which degree of crystallinity differs were made to foam, and the behavior was investigated. By 20% or less of sample, the diameter of air bubbles was set to hundreds of micrometers or more by degree of crystallinity especially 30% or less, or air bubbles have exploded. On the other hand, by 35% or more of sample, detailed foam 50 micrometers or less was obtained [ degree of crystallinity ] for the diameter of average air bubbles especially 30% or more. Therefore, in order to obtain the foam which has the detailed air bubbles of 50 micrometers or less, it is required for the degree of crystallinity of the resin before foaming to be 30% or more.

[0020] The following various approaches can be considered as an approach of making the degree of crystallinity of the thermoplastic polyester system resin in the condition of having contained non-reactivity gas 30% or more.

[0021] (1) The approach by heat treatment.

[0022] For example, in case the thermoplastic polyester system resin of the melting condition containing non-reactivity gas is extruded into another pressurized room through oil seal or mechanical seal from an extruder and it cools, the approach of making the degree of crystallinity of a resin Plastic solid 30% or more is mentioned by annealing resin, adjusting the distance from a dice outlet to a cooling roller, or the temperature of a cooling roller.

[0023] Before producing the thermoplastic polyester system resin Plastic solid which does not contain non-reactivity gas, without pouring in non-reactivity gas and making this Plastic solid contain non-reactivity gas from the extruder middle in another pressurized room, the approach of making degree of crystallinity 30% or more through a heat treating furnace may be used for behind.

[0024] (2) How to make degree of crystallinity 30% or more by making non-reactivity gas contain over long duration under pressurization.

[0025] For example, resin is once made into an amorphous state by quenching the non-reactivity gas content thermoplastic polyester system resin of the melting condition extruded in the pressurized room from the extruder. This resin Plastic solid is led to another room through oil seal or mechanical seal, and it is 10kg/cm<sup>2</sup>. Non-reactivity gas is made to contain until degree of crystallinity becomes 30% or more by the above pressure.

[0026] The approach of making non-reactivity gas containing may be used until degree of crystallinity becomes 30% or more from the extruder middle in another pressurized room, without pouring in non-reactivity gas.

[0027] (3) The approach which is immersed in an organic solvent in resin and makes degree of crystallinity 30% or more.

[0028] By quenching the thermoplastic polyester system resin of the melting condition containing the non-reactivity gas extruded in the pressurized room from the extruder, a resin Plastic solid is once made into an amorphous state. Degree of crystallinity is made into 30% or more through this resin Plastic solid into an organic solvent tub (especially acetone solvent), and the organic solvent which remains on a sheet front face by the air dried or reduced pressure drying of the bottom of un-heating, i.e., ordinary temperature, is removed.

[0029] After producing the resin Plastic solid which does not contain non-reactivity gas, without pouring in non-reactivity gas, processing this resin Plastic solid by the organic solvent and making degree of crystallinity into 30% or more from the extruder middle, a solvent is removed under un-heating and this sheet is led to another pressurized room through oil seal or mechanical seal, and it is 10kg/cm<sup>2</sup>. The approach of making non-reactivity gas containing by the above pressure may be used.

[0030] When the crystallization approach by this organic solvent is used, there is an advantage that the time amount which makes non-reactivity gas contain is shortened by about 1/10 at the maximum as compared with other approaches.

[0031] As for the upper limit of degree of crystallinity, in this invention, it is desirable that it is 50% or less. Since polyester resin will become very weak if degree of crystallinity exceeds 50%, it is not practical.

[0032] The degree of crystallinity of resin can be measured by various approaches, such as densimetry (ASTM D 1505-85), an approach by the differential scanning calorimeter (it omits Following DSC), an approach by IR, and an approach by the X diffraction. However, when the precision of equipment or the simplicity of actuation is taken into consideration, the approach by DSC is more desirable. The approach by DSC was used also about measurement of the degree of crystallinity in this invention. The calculation approach of the degree of crystallinity by DSC is described below at a detail.

[0033] First, the Plastic solid which made non-reactivity gas contain is sampled. After fully removing non-reactivity gas from this Plastic solid, by setting into DSC and carrying out a temperature up in a part for 10-degree-C/, the heating value based on crystallization and fusion of that Plastic solid is measured, and it computes based on a bottom type. If non-reactivity gas remains in a Plastic solid, non-reactivity gas will fully be removed, because there is a possibility that a Plastic solid may foam during DSC measurement and exact measurement may become impossible. In addition, according to the X diffraction by this invention persons, IR measurement, density measurement, etc., while having removed non-reactivity gas, it is clear that degree of crystallinity does not change.

[0034] Degree-of-crystallinity (%) = (A-B)/CA: The amount of heat of fusions of the C:100% crystallization [ based on fusion ] PET of heating-value B:heating values based on crystallization (117.6 J/g)

Although various values are advocated about the amount of heat of fusions of Crystallization PET 100%, the measured value by Groennickx and others is used here.

[0035] In this invention, in order to adjust the degree of crystallinity of thermoplastic polyester system resin, a crystallization nucleating additive or a crystallization accelerator may be added. As a crystallization nucleating additive or a crystallization accelerator, the denaturation polyolefine elastomer which adds and denatured the modifier to the denaturation polyolefine and the polyolefine system elastomer which add and denatured the modifier to the metal salt of inorganic compounds, such as talc, a mica, a kaolin, and a silica, the organic compound which has a carboxyl group, or a high molecular compound, and polyolefine, or an ester system plasticizer is mentioned. Furthermore, various additives, such as an anti-oxidant, an antistatic agent, an ultraviolet-rays inhibitor, a pigment, a color, and lubricant, may be blended with thermoplastic polyester system resin within limits which do not spoil the purpose of this invention.

[0036] The 3rd process is a process made to foam by heating the thermoplastic polyester system resin containing non-reactivity gas. Well-known approaches, such as an approach immersed as the approach of heating into the heat carrier set as the temperature below the melting point of resin or the approach of letting an air-heating furnace pass, can be used.

[0037] If this invention is used, by making the thermoplastic polyester system resin whose degree of crystallinity in the condition that non-reactivity gas was included is 30% or more foam, the diameter of air bubbles is controlled by 50 micrometers or less, and a mechanical strength is large and can manufacture continuously the foam which moreover does not almost have exterior irregularity.

[0038]

[Example] Hereafter, the example of this invention is explained.

[0039] The pellet of an example 1 and example of comparison 1 PET (the Unitika make, SA grade) was supplied to the extruder, and after carrying out melting kneading, it extruded in the shape of [ of 0.1mm thickness ] a sheet, and immediately after that, it quenched with the 70-degree C cooling roller, and once rolled round. The degree of crystallinity of this sheet was 5% or less. Linear velocity leads this sheet to a pressurized room through oil seal on condition that 0.1 m/min (example 1) or 0.5 m/min (example 1 of a comparison), and it is carbon dioxide gas as a

foaming agent 60kg/cm<sup>2</sup> It was made to sink in by the pressure. The residence time in a pressurized room is about 15 minutes in the example 1 of a comparison in the example 1 for about 1 hour. When degree of crystallinity was beforehand measured by DSC (product made from the SEIKO electron) about the sheet produced on these conditions, in the example 1, it was 14% in the example 1 of a comparison 36%. After taking out a sheet in atmospheric pressure through oil seal, it was made to foam [ be / it / under / warm air circulation dryer / which was set as the temperature of 240 degrees C / letting it pass ], and foam was obtained.

[0040] About the obtained foam, measurement of the diameter of average air bubbles by the scanning electron microscope (it omits Following SEM), observation of the surface irregularity by viewing, and impact strength measurement by the drop impact test were carried out. The drop impact test carried out free fall of the 12.03kg weight from the height, and the rate when colliding with a sample made it 3.9 m/sec, and it measured the maximum load concerning the load cell attached at the tip of weight at the time of a collision. These results are shown in Table 1.

[0041] The pellet of an example 2 and example of comparison 2 PET (the Unitika make, SA grade) was supplied to the extruder, and after carrying out melting kneading, it extruded in the shape of [ of 0.1mm thickness ] a sheet. The 70-degree C cooling roller was installed in the place of 50cm (example 2) or 3cm (example 2 of a comparison) for the sheet extruded from the dice from the dice outlet, cooling solidification was carried out and the sheet was once rolled round. The example 2 was [ the example 2 of a comparison of the degree of crystallinity of the sheet produced on this condition ] 3% 38%. Linear velocity leads these sheets to a pressurized room through oil seal on condition that 0.5 m/min, and it is carbon dioxide gas as a foaming agent 60kg/cm<sup>2</sup> It was made to sink in by the pressure. After coming out of these sheets into atmospheric pressure through oil seal, by letting the inside of the warm air circulation dryer set as the temperature of 240 degrees C pass, it was made to foam and desired foam was obtained.

[0042] The result of having carried out measurement of the diameter of average air bubbles by SEM, observation of the surface irregularity by viewing, and impact strength measurement by the drop impact test about the obtained foam is shown in Table 1.

[0043] The pellet of an example 3 and example of comparison 3 PET (the Unitika make, SA grade) was supplied to the extruder, and after carrying out melting kneading, it extruded in the shape of [ of 0.1mm thickness ] a sheet, quenched with the 70-degree C cooling roller immediately after that, and once rolled round. The degree of crystallinity of this sheet was 5% or less. It let the solvent tub by which linear velocity was filled with the conditions of 0.01 m/min (example 3) or 0.2 m/min (example 3 of a comparison) with the acetone in this sheet pass. The example 3 was [ the example 3 of a comparison of the degree of crystallinity at this time ] 7% 37%. This sheet is led to a pressurized room through oil seal, and it is carbon dioxide gas as a foaming agent 60kg/cm<sup>2</sup> It was made to sink in by the pressure. After taking out these sheets in atmospheric pressure through oil seal, by letting the inside of the warm air circulation dryer set as the temperature of 240 degrees C pass, it was made to foam and foam was obtained.

[0044] The result of having carried out measurement of the diameter of average air bubbles by SEM, observation of the surface irregularity by viewing, and impact strength measurement by the drop impact test about the obtained foam is shown in Table 1.

[0045]

[Table 1]

	結晶化度 (%)	平均気泡径 ( $\mu$ m)	発泡倍率 (倍)	厚 さ (mm)	落下衝撃強度 (n)	表面凹凸
実施例1	36	25	4.8	0.25	154	なし
実施例2	38	35	5.2	0.28	160	なし
実施例3	37	22	4.6	0.24	148	なし
比較例1	14	106	6.3	0.53	35	小
比較例2	3	230	8.5	0.75	23	大
比較例3	7	250	9.2	0.77	25	大

[0046]

[Effect of the Invention] As explained in full detail above, when degree of crystallinity made 30% or more of thermoplastic polyester system resin foam where a foaming agent is infiltrated, the diameter of average air bubbles contained detailed air bubbles 50 micrometers or less, and fall impact strength became possible [ obtaining good surface type-like foam greatly ].

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**TECHNICAL FIELD**

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[Industrial Application] This invention relates to the manufacture approach of thermoplastic polyester system resin foam suitable as ingredients, such as heat insulating material and a heat insulator.

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**PRIOR ART**

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[Description of the Prior Art] Before, various approaches are developed as the manufacture approach of polyester system resin foam.

[0003] After degree of crystallinity infiltrates a foaming agent into 10% or less of polyester resin, the approach of making it foam at 150-200 degrees C is indicated by JP,60-87043,A. As a reason for specifying the degree of crystallinity of resin in this official report as 10% or less, if degree of crystallinity is high, it is indicated that it is because the rate of impregnation of a foaming agent becomes low. Moreover, under foaming agent sinking in and foaming do not change, but, as for the degree of crystallinity of resin, it is indicated that crystallization advances after foaming termination. However, it is difficult to obtain detailed air bubbles, such as 50 micrometers or less, by this approach, in order the rigidity of resin is small since the degree of crystallinity of the resin at the time of foaming is as low as 10% or less, and air bubbles are large at the aforementioned foaming temperature and to grow up. In fact, in the specification, it is indicated that the diameter of air bubbles of the obtained foam is about 300 micrometers.

[0004] After carrying out melting of the aromatic polyester containing a foaming agent to JP,61-48411,B and extruding from a die, the method of manufacturing string-like aromatic polyester foam is indicated by what (it specifically cools slowly) is processed so that it may become 30% or more of degree of crystallinity of attainment degree of crystallinity.

[0005] After carrying out melting of the polyester system resin containing a foaming agent and extruding it, the approach of making the degree of crystallinity of the resin in an epidermis part 30% or less is indicated by quenching a front face compulsorily by JP,3-199243,A.

[0006] After extruding the viscous large melting resin which carried out melting of the polyester system resin (the melting property modifier is added) containing a foaming agent to JP,2-265725,A, the continuous approach of manufacturing is indicated for degree of crystallinity by quenching in 20% or less of polyester system resin foaming sheet.

[0007] The method of manufacturing polyester system resin foam is indicated by quenching, heating degree of crystallinity to it further, and making it to consider as 30% or less and it carry out post expansion, after carrying out melting of the polyester system resin containing a foaming agent and extruding it in JP,3-134037,A.

[0008] The manufacture approach of the polyester system resin foam which mixes and carries out extrusion foaming of thermoplastic polyester system resin, a melting property modifier, and the foaming agent to JP,3-266911,A, heats them to it, carries out post expansion to it, and carries out the amount of cold heat of crystallization of a post expansion object in 3000J/mol or less is indicated. In addition, since the amount of cold heat of crystallization is a fundamental value when computing the degree of crystallinity of crystalline polymer, this approach is equivalent to having essentially specified degree of crystallinity. When this invention persons convert the aforementioned amount of cold heat of crystallization into degree of crystallinity by estimate, degree of crystallinity is about 10%.

[0009] However, since foaming is advanced at the same time each of these approaches extrudes the resin of the fused amorphous state into atmospheric air from a die, it is difficult to make the diameter of air bubbles small, and the foam which has detailed air bubbles, such as 50 micrometers or less, is not obtained. Moreover, the degree of crystallinity of the foam from which

all were obtained is only specified, and the degree of crystallinity of the resin in the condition that the foaming agent sank in is not specified.

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EFFECT OF THE INVENTION

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[Effect of the Invention] As explained in full detail above, when degree of crystallinity made 30% or more of thermoplastic polyester system resin foam where a foaming agent is infiltrated, the diameter of average air bubbles contained detailed air bubbles 50 micrometers or less, and fall impact strength became possible [ obtaining good surface type-like foam greatly ].

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**TECHNICAL PROBLEM**

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[Problem(s) to be Solved by the Invention] As stated above, by the conventional approach, the diameter of air bubbles contains air bubbles 50 micrometers or less, and a mechanical strength is large, and it is difficult to obtain continuously the polyester system resin foam which does not almost have irregularity in a front face.

[0011] The diameter of air bubbles is 50 micrometers or less, and the purpose of this invention has a large mechanical strength, and is to offer the approach that the polyester system resin foam which does not almost have irregularity in a front face can be manufactured continuously.

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MEANS

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[Means for Solving the Problem] The manufacture approach of the thermoplastic polyester system resin foam of this invention The process which makes non-reactivity gas contain in thermoplastic polyester system resin under pressurization (henceforth "the 1st process"), Controlling foaming of the thermoplastic polyester system resin containing non-reactivity gas It has the process (henceforth "the 2nd process") which makes the degree of crystallinity of thermoplastic polyester system resin 30% or more, and the process (henceforth "the 3rd process") which makes the thermoplastic polyester system resin containing non-reactivity gas heat and foam to the bottom of pressureless.

[0013] Hereafter, the manufacture approach of this invention is explained to a detail for every process.

[0014] The 1st process is a process which makes non-reactivity gas contain in thermoplastic polyester system resin under pressurization. As thermoplastic polyester system resin, polyethylene terephthalate (it omits Following PET), polybutylene terephthalate, poly naphthalene terephthalate, etc. are mentioned. As non-reactivity gas, inert gas, such as an argon, nitrogen, and a carbon dioxide, air, or these mixed gas is mentioned. Also among these, a carbon dioxide is desirable, using the content to the inside of thermoplastic polyester system resin as the gas which can increase most.

[0015] This processing is performed by pouring non-reactivity gas into the thermoplastic polyester system resin of the melting condition pressurized for example, in the extruder from the barrel middle. Moreover, the approach of making non-reactivity gas containing may be used by leading the polyester system resin Plastic solid extruded for example, in the shape of a sheet from the extruder in the pressurized container filled with non-reactivity gas through mechanical seal etc. Especially pressurization conditions are 10kg/cm<sup>2</sup> at a room temperature, in order to increase the content of the non-reactivity gas to the inside of thermoplastic polyester system resin, although not limited. Considering as the above pressure is desirable.

[0016] The 2nd process is a process which makes the degree of crystallinity of the thermoplastic polyester system resin 30% or more, controlling foaming of the thermoplastic polyester system resin containing non-reactivity gas.

[0017] Since the thermoplastic polyester system resin of the melting condition containing non-reactivity gas is extruded into atmospheric air as it is by the conventional approach, it is very difficult to obtain the foam which the pressure applied to resin at the moment of come out of an extruder is released, and foaming by rapid expansion of non-reactivity gas takes place in the extruder outlet section, and has detailed air bubbles.

[0018] By the approach of this invention, without releasing the pressure to which the polyester system resin extruded, for example from the extruder was added by resin, as it is, it leads to another pressurized room, and by carrying out cooling solidification, foaming is made to control and the degree of crystallinity of the resin Plastic solid which contained non-reactivity gas in this condition is made 30% or more.

[0019] In this invention, having limited degree of crystallinity with 30% or more is based on the following reasons. According to examination of this invention persons, when crystalline polyester system resin makes non-reactivity gas contain, crystallization advances. Drawing 1 is carbon

dioxide gas as non-reactivity gas to the polyester system resin of an amorphous state 60kg/cm<sup>2</sup>. The relation of the gas sinking-in time amount and the degree of crystallinity at the time of making it contain is shown. Degree of crystallinity changes rapidly near 25 to 30%, and changes gently at 20% or less and 35% or more. And although the gas content was the same, two or more samples from which degree of crystallinity differs were made to foam, and the behavior was investigated. By 20% or less of sample, the diameter of air bubbles was set to hundreds of micrometers or more by degree of crystallinity especially 30% or less, or air bubbles have exploded. On the other hand, by 35% or more of sample, detailed foam 50 micrometers or less was obtained [ degree of crystallinity ] for the diameter of average air bubbles especially 30% or more. Therefore, in order to obtain the foam which has the detailed air bubbles of 50 micrometers or less, it is required for the degree of crystallinity of the resin before foaming to be 30% or more.

[0020] The following various approaches can be considered as an approach of making the degree of crystallinity of the thermoplastic polyester system resin in the condition of having contained non-reactivity gas 30% or more.

[0021] (1) The approach by heat treatment.

[0022] For example, in case the thermoplastic polyester system resin of the melting condition containing non-reactivity gas is extruded into another pressurized room through oil seal or mechanical seal from an extruder and it cools, the approach of making the degree of crystallinity of a resin Plastic solid 30% or more is mentioned by annealing resin, adjusting the distance from a dice outlet to a cooling roller, or the temperature of a cooling roller.

[0023] Before producing the thermoplastic polyester system resin Plastic solid which does not contain non-reactivity gas, without pouring in non-reactivity gas and making this Plastic solid contain non-reactivity gas from the extruder middle in another pressurized room, the approach of making degree of crystallinity 30% or more through a heat treating furnace may be used for behind.

[0024] (2) How to make degree of crystallinity 30% or more by making non-reactivity gas contain over long duration under pressurization.

[0025] For example, resin is once made into an amorphous state by quenching the non-reactivity gas content thermoplastic polyester system resin of the melting condition extruded in the pressurized room from the extruder. This resin Plastic solid is led to another room through oil seal or mechanical seal, and it is 10kg/cm<sup>2</sup>. Non-reactivity gas is made to contain until degree of crystallinity becomes 30% or more by the above pressure.

[0026] The approach of making non-reactivity gas containing may be used until degree of crystallinity becomes 30% or more from the extruder middle in another pressurized room, without pouring in non-reactivity gas.

[0027] (3) The approach which is immersed in an organic solvent in resin and makes degree of crystallinity 30% or more.

[0028] By quenching the thermoplastic polyester system resin of the melting condition containing the non-reactivity gas extruded in the pressurized room from the extruder, a resin Plastic solid is once made into an amorphous state. Degree of crystallinity is made into 30% or more through this resin Plastic solid into an organic solvent tub (especially acetone solvent), and the organic solvent which remains on a sheet front face by the air dried or reduced pressure drying of the bottom of un-heating, i.e., ordinary temperature, is removed.

[0029] After producing the resin Plastic solid which does not contain non-reactivity gas, without pouring in non-reactivity gas, processing this resin Plastic solid by the organic solvent and making degree of crystallinity into 30% or more from the extruder middle, a solvent is removed under un-heating and this sheet is led to another pressurized room through oil seal or mechanical seal, and it is 10kg/cm<sup>2</sup>. The approach of making non-reactivity gas containing by the above pressure may be used.

[0030] When the crystallization approach by this organic solvent is used, there is an advantage that the time amount which makes non-reactivity gas contain is shortened by about 1/10 at the maximum as compared with other approaches.

[0031] As for the upper limit of degree of crystallinity, in this invention, it is desirable that it is

50% or less. Since polyester resin will become very weak if degree of crystallinity exceeds 50%, it is not practical.

[0032] The degree of crystallinity of resin can be measured by various approaches, such as densimetry (ASTM D 1505-85), an approach by the differential scanning calorimeter (it omits Following DSC), an approach by IR, and an approach by the X diffraction. However, when the precision of equipment or the simplicity of actuation is taken into consideration, the approach by DSC is more desirable. The approach by DSC was used also about measurement of the degree of crystallinity in this invention. The calculation approach of the degree of crystallinity by DSC is described below at a detail.

[0033] First, the Plastic solid which made non-reactivity gas contain is sampled. After fully removing non-reactivity gas from this Plastic solid, by setting into DSC and carrying out a temperature up in a part for 10-degree-C/, the heating value based on crystallization and fusion of that Plastic solid is measured, and it computes based on a bottom type. If non-reactivity gas remains in a Plastic solid, non-reactivity gas will fully be removed, because there is a possibility that a Plastic solid may foam during DSC measurement and exact measurement may become impossible. In addition, according to the X diffraction by this invention persons, IR measurement, density measurement, etc., while having removed non-reactivity gas, it is clear that degree of crystallinity does not change.

[0034] Degree-of-crystallinity (%) = (A-B)/CA: The amount of heat of fusions of the C:100% crystallization [ based on fusion ] PET of heating-value B:heating values based on crystallization (117.6 J/g)

Although various values are advocated about the amount of heat of fusions of Crystallization PET 100%, the measured value by Groennickx and others is used here.

[0035] In this invention, in order to adjust the degree of crystallinity of thermoplastic polyester system resin, a crystallization nucleating additive or a crystallization accelerator may be added. As a crystallization nucleating additive or a crystallization accelerator, the denaturation polyolefine elastomer which adds and denatured the modifier to the denaturation polyolefine and the polyolefine system elastomer which add and denatured the modifier to the metal salt of inorganic compounds, such as talc, a mica, a kaolin, and a silica, the organic compound which has a carboxyl group, or a high molecular compound, and polyolefine, or an ester system plasticizer is mentioned. Furthermore, various additives, such as an anti-oxidant, an antistatic agent, an ultraviolet-rays inhibitor, a pigment, a color, and lubricant, may be blended with thermoplastic polyester system resin within limits which do not spoil the purpose of this invention.

[0036] The 3rd process is a process made to foam by heating the thermoplastic polyester system resin containing non-reactivity gas. Well-known approaches, such as an approach immersed as the approach of heating into the heat carrier set as the temperature below the melting point of resin or the approach of letting an air-heating furnace pass, can be used.

[0037] If this invention is used, by making the thermoplastic polyester system resin whose degree of crystallinity in the condition that non-reactivity gas was included is 30% or more foam, the diameter of air bubbles is controlled by 50 micrometers or less, and a mechanical strength is large and can manufacture continuously the foam which moreover does not almost have exterior irregularity.

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EXAMPLE

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[Example] Hereafter, the example of this invention is explained.

[0039] The pellet of an example 1 and example of comparison 1 PET (the Unitika make, SA grade) was supplied to the extruder, and after carrying out melting kneading, it extruded in the shape of [ of 0.1mm thickness ] a sheet, and immediately after that, it quenched with the 70-degree C cooling roller, and once rolled round. The degree of crystallinity of this sheet was 5% or less. Linear velocity leads this sheet to a pressurized room through oil seal on condition that 0.1 m/min (example 1) or 0.5 m/min (example 1 of a comparison), and it is carbon dioxide gas as a foaming agent 60kg/cm<sup>2</sup> It was made to sink in by the pressure. The residence time in a pressurized room is about 15 minutes in the example 1 of a comparison in the example 1 for about 1 hour. When degree of crystallinity was beforehand measured by DSC (product made from the SEIKO electron) about the sheet produced on these conditions, in the example 1, it was 14% in the example 1 of a comparison 36%. After taking out a sheet in atmospheric pressure through oil seal, it was made to foam [ be / it / under / warm air circulation dryer / which was set as the temperature of 240 degrees C / letting it pass ], and foam was obtained.

[0040] About the obtained foam, measurement of the diameter of average air bubbles by the scanning electron microscope (it omits Following SEM), observation of the surface irregularity by viewing, and impact strength measurement by the drop impact test were carried out. The drop impact test carried out free fall of the 12.03kg weight from the height, and the rate when colliding with a sample made it 3.9 m/sec, and it measured the maximum load concerning the load cell attached at the tip of weight at the time of a collision. These results are shown in Table 1.

[0041] The pellet of an example 2 and example of comparison 2 PET (the Unitika make, SA grade) was supplied to the extruder, and after carrying out melting kneading, it extruded in the shape of [ of 0.1mm thickness ] a sheet. The 70-degree C cooling roller was installed in the place of 50cm (example 2) or 3cm (example 2 of a comparison) for the sheet extruded from the dice from the dice outlet, cooling solidification was carried out and the sheet was once rolled round. The example 2 was [ the example 2 of a comparison of the degree of crystallinity of the sheet produced on this condition ] 3% 38%. Linear velocity leads these sheets to a pressurized room through oil seal on condition that 0.5 m/min, and it is carbon dioxide gas as a foaming agent 60kg/cm<sup>2</sup> It was made to sink in by the pressure. After coming out of these sheets into atmospheric pressure through oil seal, by letting the inside of the warm air circulation dryer set as the temperature of 240 degrees C pass, it was made to foam and desired foam was obtained.

[0042] The result of having carried out measurement of the diameter of average air bubbles by SEM, observation of the surface irregularity by viewing, and impact strength measurement by the drop impact test about the obtained foam is shown in Table 1.

[0043] The pellet of an example 3 and example of comparison 3 PET (the Unitika make, SA grade) was supplied to the extruder, and after carrying out melting kneading, it extruded in the shape of [ of 0.1mm thickness ] a sheet, quenched with the 70-degree C cooling roller immediately after that, and once rolled round. The degree of crystallinity of this sheet was 5% or less. It let the solvent tub by which linear velocity was filled with the conditions of 0.01 m/min (example 3) or 0.2 m/min (example 3 of a comparison) with the acetone in this sheet pass. The

example 3 was [ the example 3 of a comparison of the degree of crystallinity at this time ] 7% 37%. This sheet is led to a pressurized room through oil seal, and it is carbon dioxide gas as a foaming agent 60kg/cm<sup>2</sup> It was made to sink in by the pressure. After taking out these sheets in atmospheric pressure through oil seal, by letting the inside of the warm air circulation dryer set as the temperature of 240 degrees C pass, it was made to foam and foam was obtained.

[0044] The result of having carried out measurement of the diameter of average air bubbles by SEM, observation of the surface irregularity by viewing, and impact strength measurement by the drop impact test about the obtained foam is shown in Table 1.

[0045]

[Table 1]

	結晶化度 (%)	平均気泡径 ( $\mu$ m)	発泡倍率 (倍)	厚 さ (mm)	落下衝撃強度 (n)	表面凹凸
実施例1	36	25	4.8	0.25	154	なし
実施例2	38	35	5.2	0.28	160	なし
実施例3	37	22	4.6	0.24	148	なし
比較例1	14	106	6.3	0.53	35	小
比較例2	3	230	8.5	0.75	23	大
比較例3	7	250	9.2	0.77	25	大

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**DESCRIPTION OF DRAWINGS**

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[Brief Description of the Drawings]

[Drawing 1] The property Fig. showing the relation between gas sinking-in time amount and degree of crystallinity about polyester system resin.

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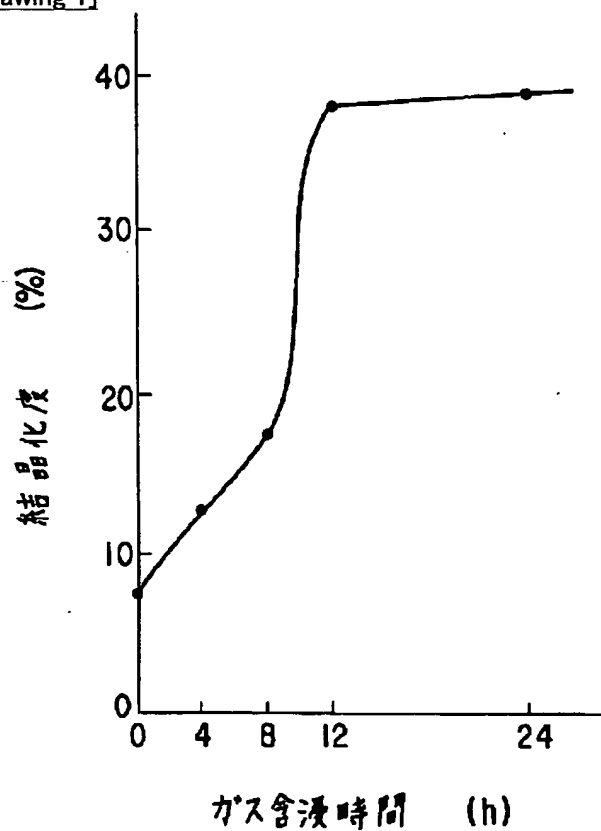
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DRAWINGS

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[Drawing 1]



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[Translation done.]